Studies on Cu and Ni doped ZnO nanocrystalline thin films by spray Pyrolysis technique

A synopsis submitted

To

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- **INTRODUCTION**

Most of the industrial materials usually called as bulk materials have fixed properties such as opacity, resistivity etc. and hence their applications are limited. For thick films or coatings that exceed the thickness of about ten micrometres their importance is nevertheless recognized. According to the studies when thickness is reduced, beyond certain limits there is drastic change in properties. This is called 'Size effect' and it adds flexibility in designing devices for several applications [1]. Thin films possess versatile properties and can have numerous applications. Devices with thin films are small in size and occupy less space, fabrication of devices requires less materials hence inexpensive.

The thin film deposition technology has improved drastically during the past 30 years. This improvement was driven mainly by need for new products and devices in the electronics and optical industries. Due to the development of new thin film deposition processes, rapid progress in solid state electronics devices would have been possible [2].

In thin film deposition, the process of nucleation and growth of thin films plays an important role. It involves three main steps:

- Production of appropriate atomic, molecular or ionic species.
- Transport of this species to the substrate through a medium.
- Lastly, condensation on the substrate either directly via chemical or electrochemical reaction to form a solid deposit.

Formation of thin films takes place via nucleation and growth process. Most of the factors of thin films are associated with growth process of the films such as structure, Crystallinity and nature of defects, for this reason suitable and non-destructive type of analytical methods should be preferred.

Semiconducting metal oxide such as TiO_2, ITO, Ga_2O_3 ZnO and SnO_2 has gain more attention because of their attractive properties such as high carrier mobility [3], non-toxicity [4] and excellent optical absorption [5]. Among these semiconducting metal oxides ZnO is most widely studied. ZnO is a n-type semiconductor material

composed of group II-VI which has a wurtzite hexagonal crystal structure. ZnO has some unique properties such as the wider direct band gap energy around 3.3 eV, the larger exciton binding energy of 60 meV and the excellent physical and chemical stability [6].These properties make it a perfect host material for optoelectronic devices like solar cells, flat panel displays, gas sensors and semiconductor lasers [7-10]. Pure ZnO has a poorly structured unit that can be repaired by doping. Appropriate donor doping can produce the electronic defects that can increase the influence of oxygen partial pressure on conductivity.

- **REVIEW OF LITERATURE**

Zinc oxide thin films are widely used in different fields of science and technologies due to their outstanding and multifunctional properties. The detailed survey of the literature of Zinc oxide (ZnO) thin films with different deposition techniques as well as its application and uses in extensively studied.

- **Gajanan Kale et.al.** [11] Studied the photo catalytic activity of Cu doped ZnO thin films. The highest photo catalytic activity was observed for Cu–ZnO with 4% doping as compared with other Cu–ZnO and ZnO nanostructure. The photocatalytic performance of Cu–ZnO shows complete degradation of MB dye within 30 min for 4% Cu–ZnO nanostructure.
- **Zohra N. Kayani et.al.**[12], study the effect of Cu doping on ZnO thin film prepared by dip coating on glass substrate. He found that increase in Cu doping leads to insignificant decrease in the optical band gap of the thin films. Also all the films show ferromagnetic properties which are due to hybridization of p–d orbital's.
- **D. Scolfaro et al.** [13] reported the investigation of the structural, morphological, and optical properties of $Zn_{1-x}Cu_xO$ thin films ($0 \leq x \leq 1$).The growth technique produced homogeneous films with increasing roughness as Cu is added. Direct and indirect band gaps were investigated as a function of Cu concentration.

- **P.S. Shewale et.al.**[14] reported the gas sensing properties of Cu doped ZnO thin films deposited by using advanced spray Pyrolysis technique. A significant response is observed towards 20ppm H_2S at 523K operating temperature for the 4 wt. % Cu doped ZnO thin films.
- **Ganesh Kumar Mani et.al.** [15] Reported Influence of copper doping on gas sensing properties of zinc oxide thin films. He observed significant amount of ammonia gas sensing response at the room temperature (303K).The Cu-doped films have much better performance than pure ZnO films with a faster response and recovery times of 30 and 14 s respectively while sensing 50 ppm of NH3.
- **M. Sh. Abdel-wahab et.al**.[16] Studied the enhanced photocatalytic activity of Ni doped ZnO thin film. The photocatalytic activities found to be increases with increasing Ni doping in to the ZnO thin films.
- **S. Yılmaz et.al.**[17] reported the structural, optical and magnetic measurements of undoped and Ni doped ZnO thin films. Magnetic measurements indicated that all the Ni-doped ZnO samples show clear ferromagnetic behaviour at room temperature.
- **W. G. Chen et.al.**[18] examined the improved acetylene gas (C_2H_2) of the Ni doped ZnO nanorods. It was found that Ni dopant is an effective additive for improving the gas response of ZnO towards C_2H_2 gas. The ZnO–Ni surface was found to absorb more C_2H_2 and receive larger electrons from adsorbed C_2H_2 molecules, which changes the electronic structure of ZnO that ultimately results in gas response enhancement.

- **<u>OBJECTIVES OF THE PRESENT WORK</u>**

The objective of the present research proposal can be summarized as follows.

- To synthesize new or improved Cu and Ni doped ZnO thin films through simple methods such as spray Pyrolysis technique.
- Investigation on the structural, morphology and optical properties of Cu and Ni doped ZnO thin films.
- The gas characteristics of the films will be investigated and reported.

- **HYPOTHESIS OF THE PRESENT WORK**
  - The research work is directed to obtain Cu and Ni doped ZnO thin films using spray Pyrolysis technique.
  - The thin films will influence the physical, morphological, magnetic and optical properties will be studied.
  - The comparative study of all grown crystals with the reported one may show the appreciable novelty in the different properties subjected to their applications in modern technological era.
  - The enhancement in optical transmission may be studied by UV visible Spectroscopy.
  - The effect of doping depends on various factors such as concentration, temperature, so it is expected to grow the crystal by varying the above parameters and to report their influence on crystal properties.

- **METHODOLOGY**

For the development and characterization of the samples following Work plan/method will be used:

I) Development of Thin Films:

It is proposed to grow Cu and Ni doped ZnO thin films by chemical Methods (Spray Pyrolysis/ Chemical Bath Deposition / SILAR). At initial stages the efforts will be done in order to deposit good quality Cu and Ni doped ZnO thin films on glass substrates.

II) Characterizations of thin films:

- **Structural characterization:** X-ray diffraction (XRD) is used for two reasons: first it provides information about the crystallographic properties of the materials. Secondly, it can be used to determine Structural parameters.

- **Morphological characterization:** The scanning electron microscope (SEM) is one of the most useful and versatile instruments for the investigation of surface topography, micro-structural features, etc.
- **Energy dispersive X-ray analysis (EDX)** is used to identify and the relative compositions of elements of samples.
- **Optical absorption spectrometry Measurement:** Optical absorption spectrometry is a very important tool to study the optical band gap of the films. Optical absorption measurements of the thin films will be carried out at room temperature in the wavelength range of 400 to 800 nm using the UV-VIS spectrophotometer. Also photoluminescence properties of the sample will be studied.
- Gas sensing Studies: Gas sensing properties of the prepared films will be measured and reported.
- Once I have the data, the analysis will take couple of months to reach the final conclusions, so that it can be published in reputed journals.

IMPORTANCE OF STUDY

- Zinc oxide (ZnO) is an n-type metal oxide semiconductor useful for optoelectronic device applications. Doping of transition metal ions (Ni, Co, Fe, Cu) into ZnO lattice can lead to modification in optical, electrical and magnetic properties.
- Nickel (Ni) has a unique chemical stability on zinc sites considers it as one of the most important doping element to tune the optical and electrical properties of ZnO.
- The replacement of Zn^{2+} ions by Ni^{2+} ions in ZnO lattice results in shrinkage of the unit cell (as ionic radii of Ni^{2+} is smaller than ionic radii of Zn^{2+}) which leads to high surface to volume ratio which can provide large number of catalytically active sites.
- Copper (Cu) is a transition metal ions which can be considered as most efficient dopant in ZnO to enhance its optical and electrical properties.

- Incorporation of Cu^{2+} ions in the ZnO lattice leads to betterment of crystalline quality which is due to difference in ionic radii of Zn^{2+} and Cu^{2+} ion.
- The Cu doping increase in donor concentration and hence a consequent changes in electrical resistivity.
- Ni and Cu doped ZnO thin films found to be promising materials for gas sensing application. The cost-effective large-scale production of these films and the development of ZnO films with improved properties are key challenges in the field of production in gas sensors.

- **CHAPTER SCHEME**

Chapter 1: Introduction of dilute magnetic semiconductor oxide thin films.

Chapter 2: Experimental and characterization techniques.

Chapter 3: Synthesis and characterization of Cu doped ZnO thin films.

Chapter 4: Synthesis and characterization of Ni doped ZnO thin films.

Chapter 5: Conclusion and future scope.

- **YEAR WISE PLAN OF WORK AND TARGETS TO BE ACHIEVE**

First year:

• Course work

• Literature review.

• Preparation of Cu and Ni doped ZnO thin films from spray Pyrolysis/CBD/SILAR technique.

• Structural Characterization.

Second year:

• Surface morphology of the prepared Cu and Ni doped ZnO thin films will be studied.

• Optical properties of the prepared samples will be studied such as photoluminescence.

Third year:

• Gas sensing properties of prepared Cu and Ni doped ZnO thin films will be studied for gs sensing applications.

• Data analysis and the results obtained will be communicated to the respective journals for publication.

• Submission of the thesis for the Doctoral degree.

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